ORGANOSILICATE MATERIALS WITH MESOSCOPIC STRUCTURES

BACKGROUND

Field of the Invention:

This invention relates to organosilicate materials.

5   Description of the Related Art:

Some techniques use structured phases of amphiphilic block copolymer molecules as templates for fabricating polymeric materials with mesoscopic structures. The block copolymer molecules self-assemble into stable structures with mesoscopic structures when their concentrations and temperatures are in specific ranges. Since block copolymer molecules have phases with different types of mesoscopic structure, these template-based techniques have been used to fabricate polymeric materials with a variety of types of mesoscopic structures.

Typical template-based methods involve several fabrication steps. The methods include making a starting solution that contains both block copolymer molecules and monomers for making the desired material. In the starting solution is a uniform solution of the two types of molecules. The methods include evaporating solvent from the starting solution until the concentration of block copolymer molecules achieves a concentration for which the stable phase for block copolymer molecules has a nontrivial mesoscopic structure. At this concentration, the block copolymer molecules self-assembly into the nontrivial structure. Self-assembly by the block copolymer molecules causes the monomers, which are intermixed with the block copolymer molecules, to also condense into a similar or different mesoscopic structure. The methods include heating the material with the mesoscopic structure to polymerize the monomers into a solid whose structure is fixed by the condensation.

The template-based methods have used alkoxide monomers to fabricate polymeric materials with a variety of morphologies. These morphologies include spherical, cylindrical, lamellae, and gyroid structures. But, the alkoxide precursors typically produce polymeric materials wettable by water.

SUMMARY

Various embodiments of template-based methods fabricate organosilicate materials with mesoscopic structures from precursors having hydrophobic moieties.

The hydrophobic moieties can cause changes to affinities towards water during curing; e.g., due to shedding of reactive hydrophilic moieties. Such changes can destroy template-induced structures, which are based on interactions between hydrophilic and hydrophobic moieties. The affinity changes can cause precursors to

5   phase separate so that the previously produced mesoscopic structures are destroyed. Curing-induced phase separations have impeded the successful use of alkoxide precursors having hydrophobic moieties in the production of materials with mesoscopic structures.

Various embodiments eliminated curing-induced destruction of mesoscopic

10   structures by using precursors that remain amphiphilic during curing. In particular, the precursors include both hydrophobic and hydrophilic moieties, and the respective hydrophobic and hydrophilic characters of these moieties are unchanged by the curing reactions that crosslink composites. Thus, crosslinking does not cause drastic changes in molecular affinities of the organosilicate precursors.

15   One embodiment features a template-based method for fabricating an organosilicate material with a mesoscopic structure. The method includes providing a solution of an amphiphilic template molecules, mixing amphiphilic organosilicate precursors into the solution to form a mixture, and evaporating solvent from the mixture. The evaporation produces a composite in which the amphiphilic

20   organosilicate precursors have a nontrivial mesoscopic structure.

Another embodiment features a solid that includes crosslinked amphiphilic organosilicate precursors. The amphiphilic organosilicate precursors form a matrix with an array of micro-structures dispersed in the matrix.

BRIEF DESCRIPTION OF THE DRAWINGS

25   Figures 1A is a cross-sectional view of a composite with an ordered array of cylindrical micro-structures therein;

Figures 1B is a cross-sectional view of another composite with an ordered array of cylindrical micro-structures therein;

Figures 1C is a cross-sectional view of another composite with an ordered

30   array of lamellar micro-structures therein;

Figure 2 is a flow chart illustrating a method for fabricating an organosilicate solid with a nontrivial mesoscopic structure;

Figure 3 is a flow chart illustrating a specific embodiment of the method of Figure 2 that is based on a sol-gel reaction;

Figure 4 shows an amphiphilic organosilicate molecule produced during prehydrolysis of a sol-gel material used in the method of Figure 3;

5   Figure 5 shows an organosilicate molecule produced by crosslinking two of the molecules of Figure 4;

Figure 6 illustrates the form of an organosilicate precursor made by further crosslinking molecules of Figure 5 during prehydrolysis of a sol-gel material; and

Figure 7 is cross-sectional view of a planar waveguide that uses a porous

10   organosilicate material produced by the method of Figure 3.

DETAILED DESCRIPTION OF EMBODIMENTS

Herein precursors are monomers or oligomers that can be crosslinked or polymerized.

Various embodiments use inhomogeneous phases of template molecules to

15   produce organosilicate materials with nontrivial mesoscopic structures. Self-assembly of the template molecules into nontrivial mesoscopic structures causes amphiphilic organosilicate precursors to arrange themselves in similar structures due to strong interactions between various portions of the two types of molecules. In particular, interactions cause either hydrophilic or hydrophobic portions of the two

20   types of molecules to assemble themselves in adjacent or overlapping physical regions.

The various embodiments avoid destruction of template-induced structure by using organosilicate precursors whose hydrophilic affinities are stable to curing. In particular, the organosilicate precursors are amphiphilic both before and after curing.

25   Thus, curing does not produce drastic changes in affinities of organosilicate molecules for water. Such drastic changes in affinities could otherwise significantly physical rearrange the precursors thereby causing a loss of mesoscopic structure during curing.

Some of the embodiments of template-based fabrication methods produce organosilicate materials that are not hydrophilic. In these materials, the presence of

30   hydrophobic moieties causes the materials to be resistant to absorption of water. In some of the materials, hydrophobic moieties of the original organosilicate precursors

are concentrated on external surfaces thereby making the materials non-wettable by
water.-

Structures of several organosilicate composites with nontrivial mesoscopic
structures are illustrated in the cross-sectional views of Figures 1A-1C. A composite

5   or solid with a nontrivial mesoscopic structure has an array of micro-structures
dispersed therein. Exemplary micro-structures include cylindrical, gyroid, lamellar,
or spherical-type structures. In composites and materials with such structures, typical
diameters of cylindrical or spherical-type micro-structures, thicknesses of lamellar
micro-structures, and inter micro-structure distances are typically in a range of about

10   2 nanometers (nm) to about 200 nm.

Figure 1A shows a composite 2 of amphiphilic organosilicate precursors and
amphiphilic template molecules, e.g., surfactants or block copolymers. The
composite 2 includes an array of cylindrical micro-structures 3 dispersed in a matrix
4. The micro-structures 3 have the same diameter, e.g., about 2 - 200 nm, and include

15   outer annular regions 5, inner annular regions 6, and cores 7. The outer annular
regions 5 and matrix 4 contain respective hydrophobic portions and hydrophilic
portions of the organosilicate precursors. The inner annular regions 6 and cores 7
contain respective hydrophilic blocks and hydrophobic blocks of the template
molecules and function as a template. The hydrophilic portions of organosilicate

20   precursors and template molecules are physically adjacent, because this physical
arrangement leads to a lower free energy under the temperature and concentration
conditions for the composite 2.

Figure 1B shows another composite 8 of amphiphilic organosilicate precursors
and amphiphilic template molecules, e.g., surfactants or block copolymers. The

25   composite 8 includes a uniform array of cylindrical micro-structures 9 dispersed in a
matrix 10. The cylindrical micro-structures 9 include annular regions 11 and cores
12. The annular regions 11 contain a uniform material containing hydrophilic
portions of both the organosilicate precursors and the template molecules. The cores
12 contain hydrophobic portions of the template molecules. The matrix 10 contains

30   hydrophobic portions of the organosilicate precursors. Hydrophilic portions of the
organosilicate precursors and the template molecules intermingle in the same physical
region, because this physical arrangement leads to a lower free energy under the
temperature and concentration conditions for making the composite 8.

Other composites and solids of amphiphilic organosilicate precursors and amphiphilic template molecules (not shown) have uniform or random arrays of spherical-type micro-structures. The morphologies of these arrays of micro-structures have the forms already shown for the arrays of cylindrical micro-structures 3, 9 in the cross-sectional views of the composites 2, 8 of Figures 1A and 1B.

Figure 1C shows a portion of an organosilicate composite 14 that includes an array of lamellae 15-18. The lamellae 15 and 16 contain respective hydrophilic and hydrophobic bocks of amphiphilic organosilicate precursors. The lamellae 17 and 18 contain respective hydrophobic and hydrophilic blocks of amphiphilic template molecules, e.g., block copolymers. In the composite 14, hydrophilic portions of organosilicate precursors and template molecules occupy physically adjacent lamellae 15, 18, and hydrophilic portions of organosilicate precursors and copolymer molecules occupy physically adjacent lamellae 16, 17. In other embodiments (not shown), either hydrophobic portions or hydrophilic portions of both types of molecules intermix in the same lamellae.

Figure 2 illustrates a method 20 for constructing an organosilicate material with a mesoscopic structure from a homogeneous solution containing amphiphilic template molecules. Herein, template molecules are molecules that tend to self-assemble into composites with nontrivial physical mesoscopic structures under certain conditions, e.g., concentration and temperature. Exemplary template molecules include small molecule surfactants and block copolymers. The type of mesoscopic structure formed by such molecules depends on the type of template molecules, the molecular concentration of the molecules, and/or the temperature.

The method 20 includes preparing a starting solution of the amphiphilic template molecules (step 22). The concentration and temperature of the starting solution is typically selected to produce a homogeneous solution of the template molecules, i.e., in a phase without a mesoscopic structure.

Method 20 also includes providing a second solution of amphiphilic organosilicate precursors, i.e., organosilicate monomers or organosilicate oligomers capable of being crosslinked (step 24). The organosilicate precursors have functional groups supporting crosslinking reactions. The organosilicate precursors also have both hydrophobic moieties and hydrophilic moieties that maintain their respective hydrophilic and hydrophobic natures under conditions of the crosslinking reactions.

Exemplary organosilicate precursors are already partially crosslinked to produce amphiphilic molecules of desired molecular weights.

Method 20 also includes mixing the two solutions to form a new solution that contains both the amphiphilic organosilicate precursors and the template molecules (step 26). The new solution is a homogeneous solution and typically does not have mesoscopic structure under the mixing conditions.

Method 20 includes evaporating solvent from the new solution, i.e., containing both the template molecules and organosilicate precursors and thereby causing the formation of a composite with a nontrivial mesoscopic structure (step 28). To produce the evaporation, the solution is heated. The evaporation causes a phase with a mesoscopic structure to become more stable than the phase in which the template molecules are homogeneously distributed in the solvent. Thus, the evaporation causes the amphiphilic template molecules physically condense or self-assemble into a composite with the nontrivial mesoscopic structure.

In the nontrivial mesoscopic structure, hydrophobic and hydrophilic blocks of the template molecules are distributed in separate physical regions. This physical separation of the hydrophobic and hydrophilic portions of the amphiphilic template molecules induces a similar physical self-assembly of the amphiphilic organosilicate precursors. The self-assemble produces a composite of both the organosilicate precursors and the template molecules, e.g., composites 2, 8, 14 of Figures 1A, 1B, or 1C. In these composites, either the hydrophilic or the hydrophobic portions of both the organosilicate precursors and template molecules are concentrated in physically neighboring or overlapping regions. The hydrophilic portions of both types of molecules occupy separate physical regions than the hydrophobic portions of these molecules.

Method 20 also includes curing the physical composite, which has a nontrivial mesoscopic structure, to form a crosslinked solid (step 30). Curing results from heating or irradiating the composite to stimulate chemical reactions among functional groups on the organosilicate precursors. These reactions produce chemical crosslinks, i.e., bonds, between the organosilicate precursors and cause the precursors to lose hydrophilic moieties. During curing, organosilicate precursors remain amphiphilic, because the precursors have both hydrophobic moieties and hydrophilic moieties that are either unreactive under the reaction conditions or react without changing their

affinities for water. Thus, curing does not cause drastic changes to affinities of the
organosilicate precursors for water. For example, curing does not change the
precursors from hydrophilic or amphiphilic molecules into hydrophobic molecules.

Eliminating drastic changes in affinities of the organosilicate precursors for
5   water is important to maintaining the template-induced mesoscopic structure as curing
progresses. Other attempts to fabricate hydrophobic materials with mesoscopic
structures from precursors with alkoxide functional groups failed, because the
precursors changed from amphiphilic to hydrophobic during curing. Prior to curing
hydrophilic portions of those precursors were physically neighboring to or intermixed
10   with hydrophilic regions of the template in composites whose organosilicate
components had nontrivial mesoscopic structures, e.g., as shown in Figures 1A, 1B,
and 1C. Nevertheless, the organosilicate precursors rearranged themselves as curing
progressed due to their drastic affinity changes. As the organosilicate precursors
became hydrophobic during curing their original physical positions near hydrophilic
15   regions of the template molecules became unstable. This caused the organosilicate
precursors to rearrange and destroyed the template-produced structure, i.e., producing
a crosslinked solid without a mesoscopic structure.

Referring again to Figure 2, method 20 also includes performing a chemical
treatment on the crosslinked solid produced at step 30 to remove part or all of the
20   block copolymer template molecules (step 32). Exemplary chemical treatments
include: burning or dissolving template molecules out of the solid, using ozonolysis to
break backbones of the template molecules thereby releasing the constituents from the
solid, or using an O_2 plasma reactive ion etch (RIE) to remove template molecules.
Removing the template molecules produces a porous organosilicate solid.

25   Figure 3 illustrates a particular method 40 for making organosilicate materials
according to method 20 of Figure 2. In the method 40, the template molecules are the
block copolymer molecules poly(butadiene)$_n$-b-poly(ethylene oxide)$_m$ (PBu-b-PEO).
In PBu-b-PEO, the poly(butadiene)$_n$ block and poly(ethylene oxide)$_m$ block are the
respective hydrophobic and hydrophilic blocks of the amphiphilic block copolymer.
30   The integers n and m, which characterize the chain length of these blocks and have
values of about 10 - 20,000 and preferably have values of about 50 - 1,000. Varying
the values of n and m enable making templates for different mesoscopic structures.

        The method 40 includes preparing a starting solution of the amphiphilic block
copolymer PBu-b-PEO (step 42). The starting solution includes about 5 weight %
PBu-b-PEO in a solvent that is an approximate 50/50 volume % mixture of
chloroform and tetrahydrofuran. The 50/50 volume % solvent mixture both dissolves
5   the block copolymer molecules and produces a solvent compatible with
prehydrolyzed sol-gel material, i.e., a prehydrolyzed sol-gel mater dissolves into this
solvent mixture. The starting solution is homogenous at the above starting weight %
concentration and room temperature.

        The method 40 also includes preparing an aqueous solution of a prehydrolyzed
10 sol-gel material, i.e., a solution of organosilicate precursors (step 44). The sol-gel
material is itself formed by reacting two silicate alkoxide monomers. One monomer
is $(CH_3)Si(OCH_2CH_3)_3$ (MTEOS), which has a hydrophobic CH_3 moiety. The other
monomer is $(CH_3O)_3Si(CH_2)_3OCH_2(CHCH_2O)$ (GLYMO), which has the hydrophilic
moiety, $(CH_2)_3OCH_2(CHCH_2O)$. The hydrophobic moiety, CH_3, and hydrophilic
15 moiety, $(CH_2)_3OCH_2(CHCH_2O)$, do not react during prehydrolysis of the sol-gel
material and do not change their respective hydrophobic and hydrophilic natures
during subsequent curing.

        Other embodiments use different silicate alkoxide silicates to prepare the sol-
gel material. Alternate silicate alkoxides for the monomer with a hydrophobic moiety
20 include methyltriethoxysilane, phenyltriethoxysilane, n-octyltriethoxysilane, and
tridecafluoro-1,1,2,2-tetrahydrooctyltriethoxysilane. Alternate silicate alkoxides for
the monomer with a hydrophilic moiety include 3-glycidoxypropyltrimethoxysilane,
mercaptopropyltrimethoxysilane (MPS), and aminopropyltrimethoxysilane (APS).

        In the exemplary embodiment, preparing the prehydrolyzed sol-gel material
25 involves mixing MTEOS and GLYMO monomers with a 15% stoichiometric amount
of water. Enough HCl is added to the solution to produce a solution whose PH in the
range of about 2 - 5. The resulting solution is stirred for about 15 minutes at a
temperature of about 273 Kelvin to start hydrolysis of the alkoxides. The hydrolysis
reaction produces primarily the amphiphilic organosilicate monomers 34 shown in
30 Figure 4. Next, the solution is heated to about 295 Kelvin and more water is added.
This causes further hydrolysis and produces the amphiphilic organosilicate molecules
36 that are partially crosslinked as shown in Figure 5. Stirring for about 1 hour

completes the hydrolysis of alkoxide groups and produces the prehydrolyzed sol-gel
material used in above step 44.

Referring to Figure 6, complete prehydrolysis produces additional crosslinking
so that the final organosilicate precursors 37 of the prehydrolyzed sol-gel solution

5   have higher molecular weights. Exemplary weights are about 2 to about 200 times
the weight of organosilicate monomer 34 of Figure 4. These partially crosslinked
organosilicate precursors 37 are still amphiphilic, because separate physical regions
38, 39 of the precursor 37 have concentrations of hydrophobic (CH_3) moieties and
concentrations of hydrophilic $OCH_2(CHCH_2O)$ moieties, respectively.

10   Referring again to Figure 3, method 40 includes mixing the prehydrolyzed sol-
gel solution with the starting solution of PBu-b-PEO to form a mixture for casting,
spin-coating, or dip-coating (step 46). After mixing, the mixture is typically stirred
for about 2 hours to get a homogeneous solution. Then, the final mixture is either
cast, spin-coated, or dip-coated on a selected substrate to produce a film of a desired

15   thickness (step 48).

The method 40 includes baking the cast, spin-coated, or dip-coated film to
evaporate remaining solvent until the PBu-b-PEO template molecules self-assemble
into a phase with a mesoscopic structure therein (step 50). The bake step maintains
the film at a temperature slightly higher than the boiling point of the solvents until the

20   solvent evaporates. Films produced by the casting, spin-coating, or dip-coating step
46 are typically thin enough so that bubbling can be avoided during the evaporation.
Bubbling could otherwise, generate cracks in the film. Exemplary evaporate
conditions for a 50/50 volume % solvent mixture of chloroform and tetrahydrofuran
involve maintaining the film at a temperature in the range of about 333 Kelvin to

25   about 343 Kelvin. At the desired PBu-b-PEO concentration, the PBu-b-PEO
molecules and the organosilicate precursors spontaneously condense to form one of
the composites 2, 8, 14 of Figure 1A, 1B, or 1C. The mesoscopic structure of the
composite depends on the concentrations of PBu-b-PEO and organosilicate
precursors, the integers n and m characterizing the chain lengths of blocks in PBu-b-

30   PEO, the molecular weights of the organosilicate precursors, and the temperature.

The method 40 also includes baking the film at a higher temperature to cause
crosslinking of the condensed organosilicate precursors and produce an crosslinked
organosilicate solid, i.e., a solid film (step 52). This higher temperature is about 403

Kelvin, and the bake is continued for a period of about 45 - 60 minutes. The bake cures the composite by producing an organosilicate solid that is fully crosslinked by siloxane crosslinks.

Since crosslinking causes the organosilicate precursors to shed alkoxide
5   functional groups, the organosilicate precursors become less hydrophilic and more hydrophobic as curing progresses. Nevertheless, curing does not cause shedding of the hydrophilic epoxide-type ($CH_2(CHCH_2O)$) moieties or the hydrophobic CH_3 moieties under the conditions of the crosslinking bake. Curing also does not change the affinities of these moieties for water. For this reason, the organosilicate
10   precursors remains amphiphilic during the bake and do not undergo a changes in their affinity for water during the cure. Avoiding changes in affinities of the precursors for water avoids destroying the previously template-produced mesoscopic structure in the organosilicate composite.

In comparison, an organosilicate composite made by a sol-gel material made
15   by hydrolyzing only $(CH_3)Si(OCH_2CH_3)_3$ monomers will have organosilicate precursors that are hydrophilic before curing and become hydrophobic, i.e., as (OCH_2CH_3) moieties are shed during curing. In a composite produced from such precursors, portions of organosilicate precursors that were intermingled with or neighboring to hydrophilic regions of block polymers during template-induced
20   formation of a mesoscopic structure will become uncomfortable with their physical locations as curing progresses. These organosilicate precursors move during curing and destroy the previously formed mesoscopic structure in the organosilicate portion of the composite. A composite of organosilicate precursors made by crosslinking the alkoxide $(CH_3)Si(OCH_2CH_3)_3$ alone will produce a cured organosilicate solid without
25   mesoscopic structure, because the organosilicate precursors become hydrophobic as their affinities for water change during the cure.

The method 40 also includes treating the crosslinked solid to chemically remove the block copolymer molecules that were previously used as a template for the mesoscopic structure (step 54). Possible treatments include burning, ozonolysis.
30   and O_2 plasma RIE. After removing the block copolymer molecules or portions the remaining solid is porous. Some embodiments leave the pores in the solid empty in applications, e.g., to make porous membranes for use as filters. Other embodiments

refill the pores with materials such as semiconductors, metals, and/or dyes for various uses.

Figure 7 is a cross-sectional view of a planar waveguide 60 that uses a porous organosilicate solid that was fabricated by method 40 of Figure 3. The waveguide 60

5   includes an optical core layer 62, an upper optical cladding layer 64, and a substrate 66 that functions as a lower optical cladding layer. The upper optical cladding layer 64 is a porous organosilicate solid that was fabricated by method 40 of Figure 3. The porous nature of upper optical cladding layer 64 produces a very low optical refractive index therein. In the upper optical cladding layer 64, exemplary refractive

10   indexes potentially have low values in the range of about 1.1 to about 1.3 due to the porous nature of the organosilicate solid. These refractive index values are lower than the approximate values of 1.3 −1.4 for refractive index that in obtainable by fluorine doping polymers. Such low refractive indexes aid to produce a high refractive index contrast between the upper optical cladding layer 64 and the optical core layer 62 of

15   the planar waveguide 60. Optical waveguides with high contrasts in refractive indexes between the optical core and cladding layers are known as a high delta waveguides. High delta waveguides are advantageous for some applications. The low refractive indexes in optical cladding layer 64 also enable using lower refractive indexes in optical core layer 62.

20   In the planar waveguide 60, the template-based fabrication process has concentrated hydrophobic moieties of organosilicate precursors on the exterior of the optical cladding layer 64. The presence of such hydrophobic moieties enables the layer 64 to protect the planar waveguide 60 from absorption of ambient water without additional protective layers. Water absorption especially into the optical core layer 62

25   could produce significant optical losses, e.g., at optical telecommunication wavelengths of about 1.3 microns to about 1.6 microns. The hydrophobicity of the upper optical cladding layer 64 eliminates the need for additional waterproof coatings to protect the optical core layer 62 from absorbing such damaging moisture.

Other embodiments of the invention will be apparent to those of skill in the are

30   in light of the specification, drawings, and claims of this application.